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Trans. of the Korean Hydrogen and New Energy Society, Vol. 33, No. 2, 2022, pp. 164~175
DOI: https://doi.org/10.7316/KHNES.2022.33.2.164

KHNES
pISSN 1738-7264 • eISSN 2288-7407

연료전지용 술폰화된 폴리(이써 이써 케톤)/스트론튬 지르코네이트 페로브스카이트 나노섬유 기반 신규 전기방사 복합막의 시너지 효과

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Synergistic Effect of Sulfonated Poly(Ether Ether Ketone)/Strontium Zirconate Perovskite Nanofiber-Based Novel Electrospun Composite Membranes for Fuel Cell Applications

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Received 2 April, 2022
Revised 25 April, 2022
Accepted 26 April, 2022

Abstract >> In this work, sulfonated poly (ether ether ketone) (SPEEK) composite membranes including strontium zirconate ($SrZrO_3$) were fabricated by the electrospinning method. Fourier-transform infrared spectroscopic analysis and X-ray diffraction analysis were used to identify the chemical structure and the crystallinity of $SrZrO_3$ and electrospun composite membranes. The thermal stability of the pure SPEEK and SPEEK/$SrZrO_3$ electrospun composite membranes were investigated by using thermogravimetric analysis. The physicochemical properties and proton conductivity were enhanced with the addition of different weight ratio of $SrZrO_3$ nanofiller (2, 4 and 6 wt%) in SPEEK polymer.
The optimized SPEEK/$SrZrO_3$-4 electrospun membrane containing 4 wt% of $SrZrO_3$ showed a high proton conductivity compared to other electrospun SPEEK/$SrZrO_3$ composite membranes. The results indicate that electrospun composite membranes incorporating these perovskite nanofillers should be explored as potential candidates for use in proton exchange membrane fuel cells.

Key words : Perovskite structure(패로브스카이트 구조), PEM(양이온 교환막), Oxidative stability(산화 안정성), SrZrO3(스트론튬 지르코네이트), Electrospun nanofiber(전기방사 나노충전제)

1. Introduction

Clean energy is a critical issue in modern society. Most of the energy is produced globally from fossil fuels, which have a negative impact on the environment worldwide. To overcome this issue, non-disruptive alternative energy conversion technologies are urgently needed[1]. As a result, fuel cells are gaining popularity because of their excellent efficiency and nearly zero emissions from fuel and oxidants[2]. In particular, the proton exchange membrane fuel cells (PEMFCs) provide high-efficiency and eco-friendly energy that uses hydrogen and air as fuels to generate electricity via a chemical reaction and produces water as a by-product.

The main component of the PEMFCs is the proton exchange membrane (PEM), which transports protons between the electrodes and prevents the mixing of H_2 and O_2 gases[3-6]. At presently, perfluorinated sulfonic acids such as Nafion are the principle material because of their high ionic conductivity and excellent mechanical stability and durability. However, it has a significant disadvantage such as low proton conductivity at high temperature, difficulty in operation at low relative humidity, and high price[7,8].

In order to solve aforementioned problems, intensive efforts are being focused on improving the low-cost aromatic proton conducting polymer membranes that can replace Nafion. Numerous studies show that the incorporation inorganic fillers into polymers can improve the polymer structure, physicochemical properties, thermal stability, permselectivity and mechanical properties, and the pore structure and size distribution of the membranes[9,10]. Such aromatic proton conducting polymers include sulfonated poly(ether sulfone) (SPES), sulfonated poly (ether ether ketone) (SPEEK), sulfonated poly(1,4-phenylene ether ether sulfone) (SPEES), sulfonated poly (benzimidazole) (SPBI) and sulfonated poly(vinyl alcohol) (SPVA) are intensively used in PEMFC applications[11-13].

Currently, organic-inorganic electrospun polymer composite materials are receiving much attention due to their excellent structural, physicochemical, thermal, and electrochemical properties. In particular, SPEEK is a proton conducting polymer in nature that can easily control proton conductivity and thermochemical properties by changing the degree of sulfonation (DS). The SPEEK is an aromatic hydrocarbon polymer and its nanofiber morphology can be predicted to improve chemical stability and high proton conductivity through electrospinning. The electrospun polymer composites systems can improve the properties of PEMFC. It provides improved membrane stability and proton conductivity compared to solvent casting[14].

In the current investigation, the incorporation of ABO_3 perovskite oxides is structurally strong due to its high temperature proton conductivity compared to normal hygroscopic oxides. Strontium zirconate ($SrZrO_3$) is a perovskite material with a pseudocubic in the *Pbnm* space group. Strontium zirconate is a mixed metal oxides with different structural characteristics, and due to its proton conductivity at high temperatures, it can be widely applied in the field of electronic ceramics and high melting temperature refractory materials, and in the fields of fuel cells and hydrogen sensors. This material exhibits excellent structural and morphological behavior and large metal-oxygen bonding energy.

According to the Lewis acid-base theory, Sr^{2+} and Zr^{4+} act as hard acids that react with the -OH group of water molecule. The pseudocubic perovskite of $SrZrO_3$'s has attracted attention due to its excellent proton transport ability and ability to generate a strong oxygen deficient vacancy ($0<\delta<0.5$). The oxygen vacancies mentioned above are very good for attracting water molecules (H_2O) that have been changed to their hydroxyl form (OH) and transporting protons along the lattice[15,16].

In the literature, Lee et al.[17] impregnated SPEEK/silicon dioxide (SiO_2) nanofibers in Nafion to create a strong pore-filled membrane, which prevented the matrix from swelling (3.3%) at high temperatures (75°C). Salleh et al.[18] reported that SPEEK/Closite 15A electrospun polymer composites provided better proton conductivity (80°C), oxidative stability and better electrochemical performance compared to the pure SPEEK electrospun composite membrane. Raja Pugalenthi et al.[19] described a SPEEK/$SrFeO_3$ proton conducting electrospun membranes, which provides proton conduction (95 mS cm^{-1} at 80°C) and cell performance (342 mW cm^{-2}). These results indicate that the inclusion of $SrFeO_3$ in SPEEK matrices has better properties than the cast SPEEK membranes under hydration conditions. Choi et al.[20] synthesized strong SPEEK nanofibers with carbon nanotubes (CNTs) to construct a highly efficient nanophase linked polymer membrane. They have a higher Young's modulus (615 MPa) than pure SPEEK (557 MPa) and better performance at 80°C (1.1 W cm^{-2}) than pure SPEEK (0.8 W cm^{-2}).

Based on the above inspiration, we prepared SPEEK/$SrZrO_3$ electrospun composite membranes by electrospinning method. The electrospun composite membranes prepared with various wt% $SrZrO_3$ in SPEEK matrix were analyzed in terms of ionic conductivity, water uptake, and ion exchange capacity. The structural and morphological properties of SPEEK/$SrZrO_3$ electrospun composite membranes were determined using Fourier-transform infrared (FT-IR), XRD, ^{1}H NMR and SEM analysis. The obtained electrospun composite membranes exhibited excellent proton conductivity, high thermal stability and chemical stability, suggesting that it is suitable as electrolytes for PEMFC applications.

2. Experimental

2.1 Reagents and chemicals

Poly(ether ether ketone) (PEEK) were obtained from Solvay chemicals PVT, Gujarat, India. Concentrated sulfuric acid (H_2SO_4, 98%), N,N-dimethylformamide (DMF, 95%), acetone (98%), strontium nitrate ($SrNO_3$, 98%), sodium hydroxide (NaOH, 97%), sodium chloride (NaCl, 99%), zirconium nitrate ($ZrNO_3$, 99%), potassium hydroxide (KOH, 94%), hydrogen peroxide (H_2O_2, 30% v/v) were purchased from Sigma-Aldrich, Mumbai, India. All experiments were carried out using deionized (DI) water.

2.2 Synthesis of SPEEK

PEEK was sulfonated via a previously reported classical method[21]. The PEEK powder was dried in a vacuum oven before reaction. 10 g of dried SPEEK was slowly mixed to 150 mL of conc. H_2SO_4, and

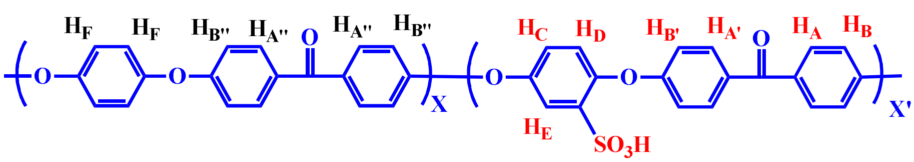

Fig. 1. Chemical structure of SPEEK polymer

then solution was stirred at 40°C for 7 hours and the polymer solution was precipitated in cold water to complete the sulfonation. The yellow precipitate was washed repeatedly with DI water until a neutral pH was reached.

The SPEEK (Fig. 1) with the following ^{1}H NMR data was produced in approximately 90% yield: ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.9-7.70 (H_A, $H_{A'}$, $H_{A''}$, 8H), 7.6-7.45 (H_E, 1H), 7.3-7.2 (H_F, H_D, 5H), 7.2-7.05 ($H_{B'}$, $H_{B''}$, H_C, 7H), 7.05-6.95 (H_B, 2H).

2.3 Synthesis of $SrZrO_3$ nanoparticles

1 M strontium nitrate, 1 M zirconium nitrate and 0.5 M potassium hydroxide were mixed together in a 1:1 ratio and stirred for 12 h. The centrifugation process was manipulated to separate the solid particles from the remaining solvent. The obtained powder was calcined by 900°C.

2.4 Preparation of SPEEK/$SrZrO_3$ electrospun composite membranes

Electrospun membranes containing 0, 2, 4 and 6 wt% of $SrZrO_3$ perovskite filler and named as SPEEK, SPEEK/$SrZrO_3$-2, SPEEK/$SrZrO_3$-4 and SPEEK/$SrZrO_3$-6, respectively. To start, SPEEK was added to 5 mL of DMF with vigorous stirring at 30°C for 24 h. Then, a sufficient amount of $SrZrO_3$ was distributed in the polymer solution using sonication and stirring at 80°C for 24 hours. Using an ectrospinning technique, nanofibers were made from a prepared polymer solution. Electrospinning of the solution was carried out at a voltage of 22 kV and a flow rate of 0.3 mL h^{-1}.

The electrospun membrane was received on a spinning drum at a speed of 1500 revolutions per minute and covered with aluminum foil (at the distance of 11 cm from syringe spout). The electrospun composite membrane was dried at 70°C for 9 hours to reduce any residual solvent. The thicknesses of the prepared electrospun composite membranes were calculated in the range of 30 and 40 μm using a digital micrometer. The aforementioned process is shown in Fig. 2.

Each SPEEK/$SrZrO_3$ electrospun membrane was impregnated with 10 mL of a solution of 5 wt% Nafion in 5 mL isopropanol with 0.5 mL water (3/2, w/w), respectively. Finally, the prepared electrospun membranes were immersed in 0.5 M H_2SO_4 for the activation process.

2.5 Characterization

FT-IR spectra of the electrospun composite membranes were taken between 4000 and 400 cm^{-1} on a (FT-IR, Perkin Elmer, Waltham, USA). The phase structure of the electrospun composite membranes was characterized using a powder X-ray diffractometer (PXRD, X'Pert MRD with Cu Kα radiation). ^{1}H NMR

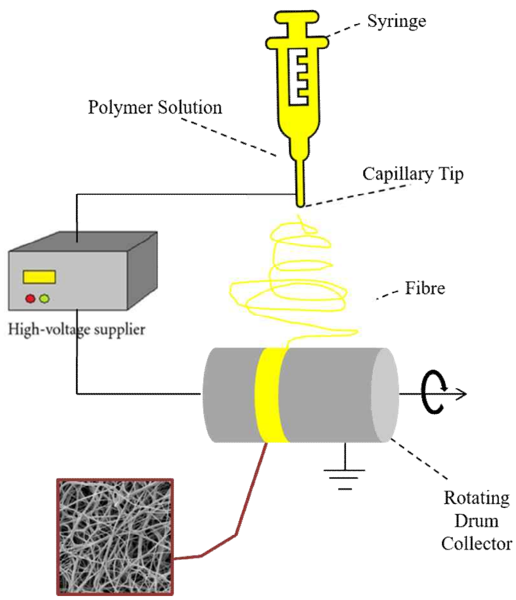

Fig. 2. Electrospinning process for SPEEK/$SrZrO_3$ electrospun membranes

was recorded on a Bruker 400 MHz NMR spectrometer.

The morphological behavior of the electrospun composite membranes was investigated using a scanning electron microscope (SEM, SUPRA 40VP). The thermal stability of the electrospun membranes was determined using thermogravimetric analysis (TGA) model (Q 50) heating in an N_2 environment at 10°C min^{-1}.

The proton conductivity of the prepared electrospun composite membranes was evaluated from a Nyquist plot obtained from impedance measurements of a computer-controlled micro auto lab type III potentiostat/Galvanostat with a signal amplitude of 10 mV and a frequency range of 10 Hz～10 MHz. The proton conductivity (σ) was then calculated using the Nyquist plot and the electrolyte resistance (R_b) determined by the intersection of the X-axis, the membrane thickness (L) and the electrode area (A) according to the equation (1):

$$\text{Proton conductivity } (\sigma) = L/AR_b \quad (1)$$

The water uptake of electrospun composite membranes was measured by the change in weight of the electrospun composite membranes having a size of 1 cm×1 cm, and then immersed in DI water at 30°C for 24 h to maintain the equilibrium state. After elimination of surface water for 24 hours, the electrospun membranes were quickly weighed and the results recorded. The water uptake of the membranes was calculated using equation (2):

$$\text{Water uptake } (\%) = \frac{W_{wet}-W_{dry}}{W_{dry}} \times 100 \quad (2)$$

The ion exchange capacity(IEC) of the electrospun composite membranes was determined using a back-titration approach. To begin, the acidic membranes (H^+) were converted to the Na^+ form by immersion in 1 M NaCl solution at 30°C for 24 hours. Then, the H^+ ions exchanged in the solution were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. Finally, the IEC was calculated as in the following equation (3):

$$\text{IEC (meq/g)} = \frac{V_{NaOH}(mL) \times C_{NaOH}(M)}{m_{dry}(g)} \quad (3)$$

In addition, the chemical stability of the prepared composite membranes was evaluated through the Fenton's test. The electrospun composite membrane obtained here was initially soaked in Fenton's regent (3 ppm of $FeSO_4$ with 3% H_2O_2 solution) at 80°C for 134 hours. The resultant membrane was then dried at 80°C, and the initial and final weight loss was calculated.

3. Results and Discussion

3.1 ^{1}H NMR study

The ^{1}H NMR spectra of the prepared SPEEK was measured using DMSO-d_6 solvent. These proton signals are in good agreement with those reported pre-

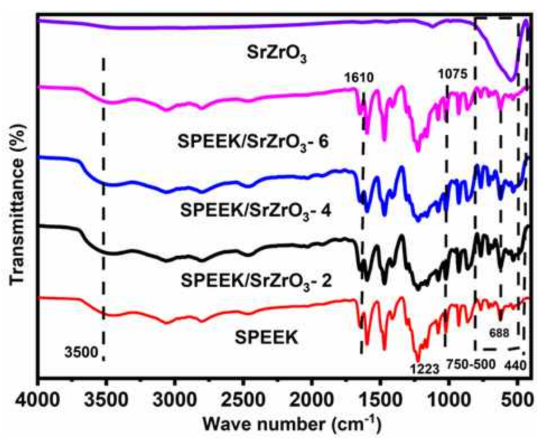

Fig. 3. FTIR spectra of pristine SPEEK, $SrZrO_3$ and prepared electrospun composite membranes

viously[22]. The DS of SPEEK was 65%.

3.2 FT-IR study

Fig. 3 shows the FT-IR spectrum of pristine SPEEK, $SrZrO_3$ and electrospun membranes SPEEK/$SrZrO_3$-2, SPEEK/$SrZrO_3$-4 and SPEEK/$SrZrO_3$-6. In the vibrational spectrum of SPEEK there was a broad peak in the region 3500 cm^{-1} confirming the OH stretch of SO_3H group of SPEEK. In the spectrum of $SrZrO_3$, two vibrational peaks were observed at 440 cm^{-1} and 533 cm^{-1}, which correspond to the presence of Zr-O and Sr-O stretching vibration modes in $SrZrO_3$, respectively[16].

FT-IR analysis of the SPEEK/$SrZrO_3$ electrospun membranes shows that the intensity of bending vibration of the hydroxyl group at 1610 cm^{-1} and 3,500 cm^{-1} increases with increasing filler content in $SrZrO_3$ due to the additional hydroxyl groups present in the filler[23]. The observed vibrational peaks at 400 ~750 cm^{-1} of the prepared electrospun composite membranes indicate the metal-oxygen stretching vibrations at the B site of ABO_3 perovskite[24]. The above results confirm that the SPEEK/$SrZrO_3$ composite is formed by hydrogen bonding between the SPEEK sulfonic acid group and the $SrZrO_3$ functional group.

3.3 XRD analysis

XRD analysis is a powerful tool for determining the structural behavior. Fig. 4 shows the XRD patterns of pristine SPEEK, pristine $SrZrO_3$ and prepared electrospun composite membranes. In Fig. 4, the pure SPEEK membrane exhibited a wide centered peak at 2θ=20°, confirming the semi-crystalline structure. It confirms the loss of crystallinity and chain conformation[25]. The pure $SrZrO_3$ exhibits five major peaks at 2θ=30.85º, 44.13º, 54.66º, 63.89º and 72.54º represents the crystal planes of (002), (040), (240), (242), and (323)[16]. The average particle size was calculated by using the Scherrer's equation as follows.

$$D = \frac{0.9\,\lambda}{\beta\,Cos\theta} \tag{4}$$

λ = X-ray wavelength, β = full-width half maximum, θ = diffraction angle

The average particle size of the $SrZrO_3$ nanoparticles was found to be 55 nm. The SPEEK membrane and SPEEK/$SrZrO_3$ electrospun composite membranes exhibit a broad diffraction peak between 20~30º indicating the amorphous nature. The peak intensity at 6 wt% $SrZrO_3$ increases in the prepared electrospun membranes due to the agglomeration effect of $SrZrO_3$ occurring in the electrospun membrane.

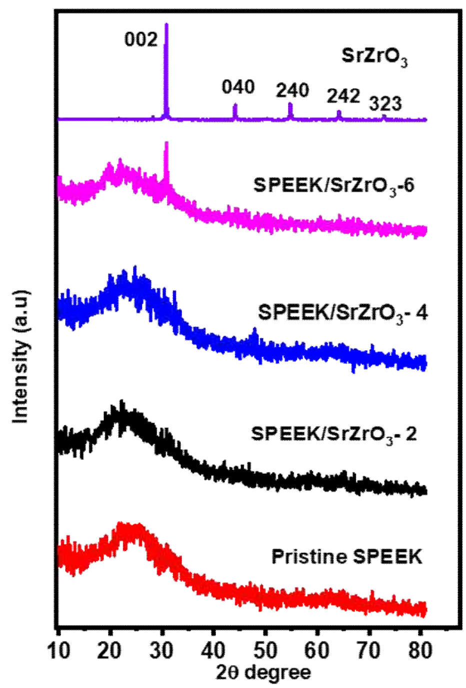

Fig. 4. XRD patterns of pristine SPEEK, $SrZrO_3$ and prepared electrospun composite membranes

3.4 Water uptake, ion exchange capacity and oxidative stability

Water up take is one of the important properties for fuel cell system operation. Increased water uptake by electrospun membrane can promote better proton transport[26-28]. The water uptake of electrospun composite membranes generally increases with increasing IEC properties due to their increased hydrophilic nature. The $SrZrO_3$ fillers increased the water retention capacity of SPEEK membranesr. The water uptake was performed at 30°C and the obtained values were calculated according to equations (2) and (3), and the corresponding calculation results are shown in Table 1. As a result, the water uptake values for all the manufactured electrospun membranes were greater than those of pure SPEEK electrospun membranes. Table 1 shows that the prepared SPEEK/$SrZrO_3$-4 electrospun membrane demonstrated the highest water uptake value of 17.34%, which is more reasonable for the utillization of the operating electrospun membranes in fuel cells under humid conditions.

In addition, IEC is one of the major properties of proton conducting polymers, which can be improved by adding ion exchange fillers. The pure SPEEK electrospun membrane exhibited an IEC of 1.2 meq g^{-1} as a result of contribution by sulfonic acid group (SO_3H). Increasing the amount of $SrZrO_3$ in the SPEEK electrospun membrane increased the ion exchange capacity as shown in Table 1. A maximum IEC of 2.5 meq g^{-1} was shown by the SPEEK/$SrZrO_3$-4 electrospun membrane. Whereas, the SPEEK/$SrZrO_3$-6 electrospun membrane showed lower IEC values due to the agglomeration of $SrZrO_3$ particles, which blocks the ion exchange groups from participating the ion exchange process.

The chemical stability of prepared electrospun composite membranes as estimated using Fenton's reagent method is one of the essential prerequisites for the fuel cell operation. The pure SPEEK electrospun membrane and the prepared electrospun composite membrane showed a weight loss of less than 6 wt% after immersion in Fenton's reagent for 134 hours (Fig. 5). This shows that the electrospun membranes have good chemical stability. Disruption of the ether-bonded

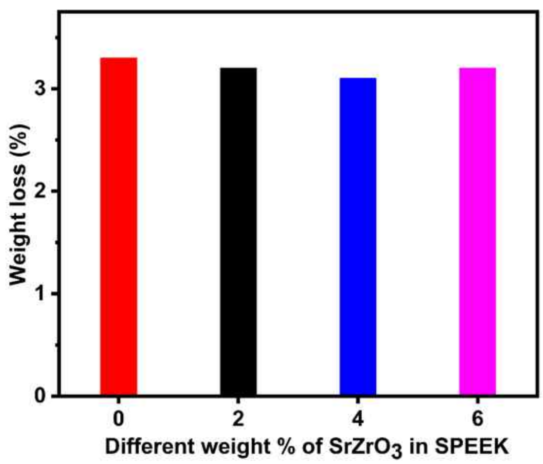

Fig. 5. Oxidative stability of SPEEK and the prepared electrospun composite membranes

Table 1. Water uptake, IEC and proton conductivity values for the prepared electrospun composite membranes

S. No	Electrospun composite membranes	Water uptake (%) 30°C	IEC (meq g^{-1})	Proton conductivity (S cm^{-1}) at 30°C
1	SPEEK	14.42	2.0	6.43×10^{-2}
2	SPEEK/$SrZrO_3$-2	16.32	2.3	9.15×10^{-2}
3	SPEEK/$SrZrO_3$-4	17.34	2.5	13.62×10^{-2}
4	SPEEK/$SrZrO_3$-6	16.12	2.2	10.14×10^{-2}

SPEEK polymer chains can cause a decrease in the stability of the electrospun membrane.

3.5 Thermal stability

The thermal stability of the prepared electrospun membranes was investigated using TGA analysis at heating rate of 10 °C min^{-1} in an N_2 atmosphere. The TGA curve of prepared electrospun membranes is shown in Fig. 6. Pure SPEEK and prepared SPEEK/$SrZrO_3$ electrospun membranes show the first loss corresponding to moisture on sample loading[29]. The second weight loss occurring at 250～400°C is caused by the degradation of the sulfonic acid group (SO_3H) in the prepared electrospun membranes[30]. The rapid third weight loss occurring at 400～800°C proceeds with the decomposition of aromatic chains of sulfonated polymers bound to the pure SPEEK electrospun membrane, and the prepared electrospun membrane exhibits delayed behavior of the weight droplets[31,32].

The TGA curves of electrospun composite membranes showed a slightly delayed weight loss compared to the pure SPEEK due to the electrostatic interactions between the $SrZrO_3$ and -SO_3H groups of SPEEK electrospun membrane. The obtained results demonstrate that TGA shows high thermal properties of the SPEEK/$SrZrO_3$-4 electrospun composite membrane for PEMFC applications.

3.6 Morphology study

The surface morphologies of the pristine SPEEK (casted and electrospun), pure $SrZrO_3$ and prepared electrospun membranes are represented in Fig. 7. Fig. 7A shows the smooth and uniform surface morphology of a pore-free SPEEK(cast) membrane. The SEM images of SPEEK and SPEEK/$SrZrO_3$ electrospun membranes are shown in Fig. 7B～E. The filler particles are dispersed in a homogeneous pattern (fibers) and are clearly embedded in the SPEEK polymer matrix[33]. The $SrZrO_3$ particles are well dispersed in the SPEEK matrix without aggregation in the prepared electrospun because there is a strong electrostatic attraction with sulfonic acids (SO_3H) between $SrZrO_3$ and SPEEK. The results obtained were similar to those of previous works[34,35].

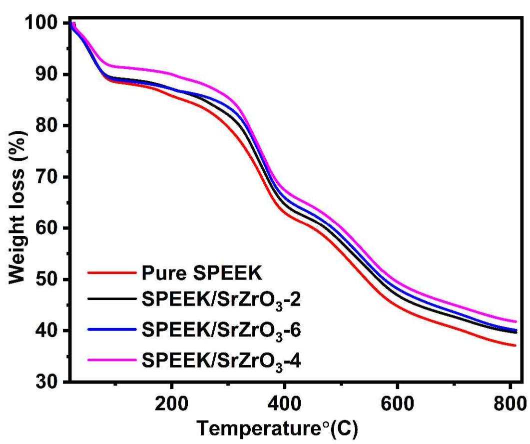

Fig. 6. TGA plot for pure SPEEK, SPEEK/$SrZrO_3$-2, SPEEK/$SrZrO_3$-4 and SPEEK/$SrZrO_3$-6

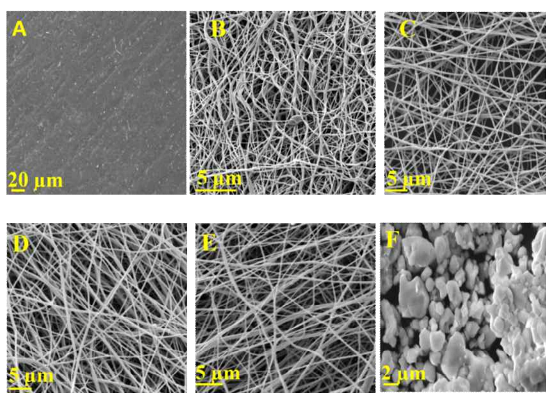

Fig. 7. FE-SEM images of (A) SPEEK (cast), (B) SPEEK (electrospun), (C) SPEEK/$SrZrO_3$-2, (D) SPEEK/$SrZrO_3$-4, (E) SPEEK/$SrZrO_3$-6, and (F) $SrZrO_3$

3.7 AC impedance

The Nyquist plot of SPEEK, SPEEK/$SrZrO_3$-2, SPEEK/$SrZrO_3$-4 and SPEEK/$SrZrO_3$-6 at 30°C are shown in Fig. 8. According to Fig. 8, the real part of the x-axis is denoted by Z' and the imaginary part is denoted by -Z''. The bulk resistance R_b can be calculated from the intercept on the x axis. The proton conductivity was calculated from the bulk resistance of the electrospun membranes of Fig. 8 using equation (1). The SPEEK electrospun membrane achieved a conductivity of 6.43×10^{-2} S cm^{-1} at 30°C. Compared to this membrane, the SPEEK/$SrZrO_3$-4 electrospun membrane increased the conductivity up to 13.62×10^{-2} S cm^{-1} at 30°C due to highly conductive electrospun composite membrane. Increasing the amount of filler particle in the SPEEK electrospun membrane increased the proton conductivity as shown in Table 1.

The proton conductivity of electrospun membrane is enhanced by two possible factors, such as the excessive concentration of ion-conducting SO_3H provided by the high surface area of $SrZrO_3$ nanoparticles and the intrinsic ability of $SrZrO_3$ nanoparticles to retain their physical and chemical properties[36-39]. In $SrZrO_3$, proton transport is facilitated by hydrogen bonding between adjacent lattice oxygen atoms and reorientation of related oxygen sites. The oxygen site of Zr-O-Zr lowers the energy barrier for ion transport and large cation at the A-site contributes to a reduced activation enthalpy for ion mobility[40,41].

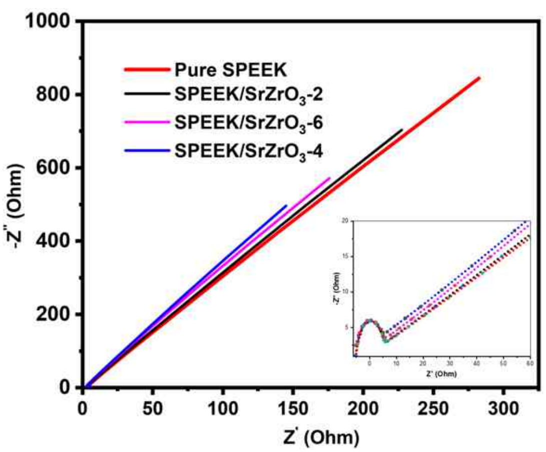

Fig. 8. Nyquist plot for pure SPEEK and prepared electrospun membranes at 30°C

The incorporation of the $SrZrO_3$ increases the water adsorption properties of SPEEK electrospun membrane, and the adsorbed water molecules increase the size of ion cluster domains and the strong interconnection and dissociation of acidic functional groups. For membranes with 6 wt% $SrZrO_3$ filler, a slight decrease in proton conductivity was observed due to particle agglomeration disrupting the ionic channel of the electrospun membrane.

4. Conclusions

The present study described aspects of $SrZrO_3$ perovskite in SPEEK electrospun membranes as electrolytes for PEMFC applications. The synthesized $SrZrO_3$ and the prepared electrospun membranes were characterized by NMR, XRD, FTIR, TGA, and SEM to investigate their physicochemical properties.

In the presence of $SrZrO_3$, the SPEEK electrospun membranes showed better physicochemical properties and proton conductivity compared to the pristine SPEEK. The electrospun with 4 wt% of $SrZrO_3$ showed the best results compared to other electrospun composite membranes. The highest proton conductivity was obtained at 13.62×10^{-2} S cm^{-1} at 30°C for SPEEK/$SrZrO_3$-4 electrospun composite membrane. The aggregation and blocking effect of $SrZrO_3$ at 6 wt% of the $SrZrO_3$ filler reduced the proton conductivity. Therefore, the SPEEK/$SrZrO_3$-4 based electrospun composite membrane is a promising electrolyte for PEMFC applications.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2020R1A 2B5B01001458). This research was supported by Basic Science Research through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2021R1I1A1A01050905).

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